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VITRIFICATION OF HIGH-LEVEL ICPP CALCINED WASTES

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ABSTRACT

A flux which will mix with ICPP high-level calcined zirconia waste to form a low-viscosity leach-resistant glass at 1100°C was developed. Effects of each of the glass additives Na_2O, B_2O_3, Li_2O, ZnO, CuO, and P_2O_5 are compared on the basis of leach resistance and viscosity. Methods to analyze fluoride content were developed.

A glass forming flux containing 2% CuO, 24% Na_2O, 8% B_2O_3, and 66% SiO_2 was chosen for its ability to produce a highly leach-resistant (0.20 wt% lost at pH 3.7 and 25°C after 19 hours) waste glass and its ability to accept a wide range of waste loadings (25-40 wt% calcine in the final glass).

SUMMARY

Long-term storage of high-level wastes may require a mechanically non-dispersible and chemically leach resistant form. One method under consideration is to vitrify calcined waste into a leach-resistant glass which would contain 25 to 40% calcine. A full-scale process to vitrify defense waste at the Idaho National Engineering Laboratory (INEL) could process all of the existing high-level calcined waste and that produced in a 10 year period after process initiation. The process would vitrify zirconia, alumina, stainless-steel, and Zr-Na blend calcines produced at the Idaho Chemical Processing Plant (ICPP).

Glasses of 116 compositions were made with simulated zirconia waste and compared on the basis of viscosity at the melting temperature and gross weight loss in an acid leach. The glasses were primarily borosilicates with minor additives (1-5 wt%) of Li_2O, P_2O_5, CuO, and ZnO to the SiO_2, Na_2O, B_2O_3 matrix. The experimental glasses compared many combinations of these additives at varying concentrations and at melt temperatures of 1050 to 1200°C, and waste loadings of 25 to 40 wt% calcine.

Glasses had a density of 2.5 to 2.75 g/cm^3 and softened at about 520-570°C. Fluoride volatility was 5 to 20% at the 1100°C melt temperature. The crystalline content ranged from 1 to 8 wt% and consisted primarily of CaF_2. Crystalline CaF_2 concentration decreases over at least the first 2 weeks when the glass is kept at 700 to 800°C, but other crystalline forms appear as the glass devitrifies. Soxhlet leach rates did not change significantly.

The most promising glass on the basis of low melt viscosity at 1100°C and high leach resistance is a glass containing 44% SiO_2, 16% Na_2O, 5.33% B_2O_3, 1.33% CuO, and 33.34% zirconia calcine. This glass (No. 51) can also incorporate variations up to 20% in alumina and up to 15% dolomite (a calcining startup material) with no significant deterioration of quality.

Further testing of effects of devitrification on leach resistance and mixed alkali and Fe_2O_3 effects on viscosity and leach resistance are underway.

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I. Introduction

The Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory (INEL) reprocesses defense type nuclear fuel using a solvent extraction process.[1] The resulting high-level waste solution is calcined (dried) in a fluidized-bed process into a mixture of granules and powder known as calcine.[2]

Calcine is currently stored on site at the ICPP in stainless steel bins.[3] However, should permanent storage or disposal at an off-site Federal repository be required, calcine would be evaluated to meet shipping and repository criteria. The possibility of dispersion of the calcine by air or water in the event of a shipping spill makes consolidation of the calcine an attractive alternative. Once in the repository high-level-form criteria may require multiple barriers, one of which may be a leach resistant material such as glass, which has been shown to be leach resistant in certain ground-waters.[4] The major reasons for vitrifying a high-level waste, therefore, are to make it less dispersible and more leach resistant than calcine to improve isolation of the radioactivity from the biosphere.

This report discusses the work done to date at the ICPP on the vitrification of calcined ICPP waste and characterization of the glass. Vitrification is one of several waste management alternatives being investigated at the ICPP.[5]

Alternatives to vitrification of the waste include pelletization, actinide removal, on-site glass storage, stabilization of the calcine for shipment to a repository, and leaving the calcine in its present form on-site.

II. Conceptual Vitrification Process

Full-scale practical application of the waste vitrification process sets many of the requirements on the physical characteristics of the glass. One potential process consists basically of feeding glass forming additives and calcine directly to a ceramic melter.[6] The melter would operate continuously, tipped intermittently or constantly, to pour glass directly into storage canisters (as shown in Figure 1). For smooth pouring, the glass must have a viscosity of less than 500 poise at the operating temperature. To have reasonable refractory and electrode service lifetimes, the maximum allowable melting temperatures should be 1100-1200°C. In addition, volatility of fission products and fluorides are minimized with lower melting temperatures. These conditions limit the possible glass compositions since a high silica content or low alkali content require high melting temperatures to produce a low viscosity glass. The process must be designed to operate with simplicity since all maintenance and operation will be done remotely.

An alternative glass process, "in-can melting", is also being considered.[7] In this process a canister is heated directly while the glass frit and calcine are fed to the canister. Since the canister itself acts as the melter, the glass is never poured and viscosities need only be low enough to allow escape of gases and adequate mixing, though these considerations may require fairly low viscosities. In addition, each canister acts as a new melter so long-term corrosion by the glass need not be considered. The canister may be contained in an overpack; therefore, it must only withstand the corrosion incurred during the heating time and the hydraulic pressure of the molten glass. Since the glass melting rate with this method is slow, several process lines would be needed to meet ICPP processing goals. At present, design work is based on a throughput of $\sim$14 tons of glass per day which would reduce the calcine inventory at the time of estimated startup in 1992 to a plant operating level in a 10 year period. After that time the processing rate would match the throughput of the calciner at the ICPP. After casting, the canisters would be temporarily stored before shipment to a Federal repository.

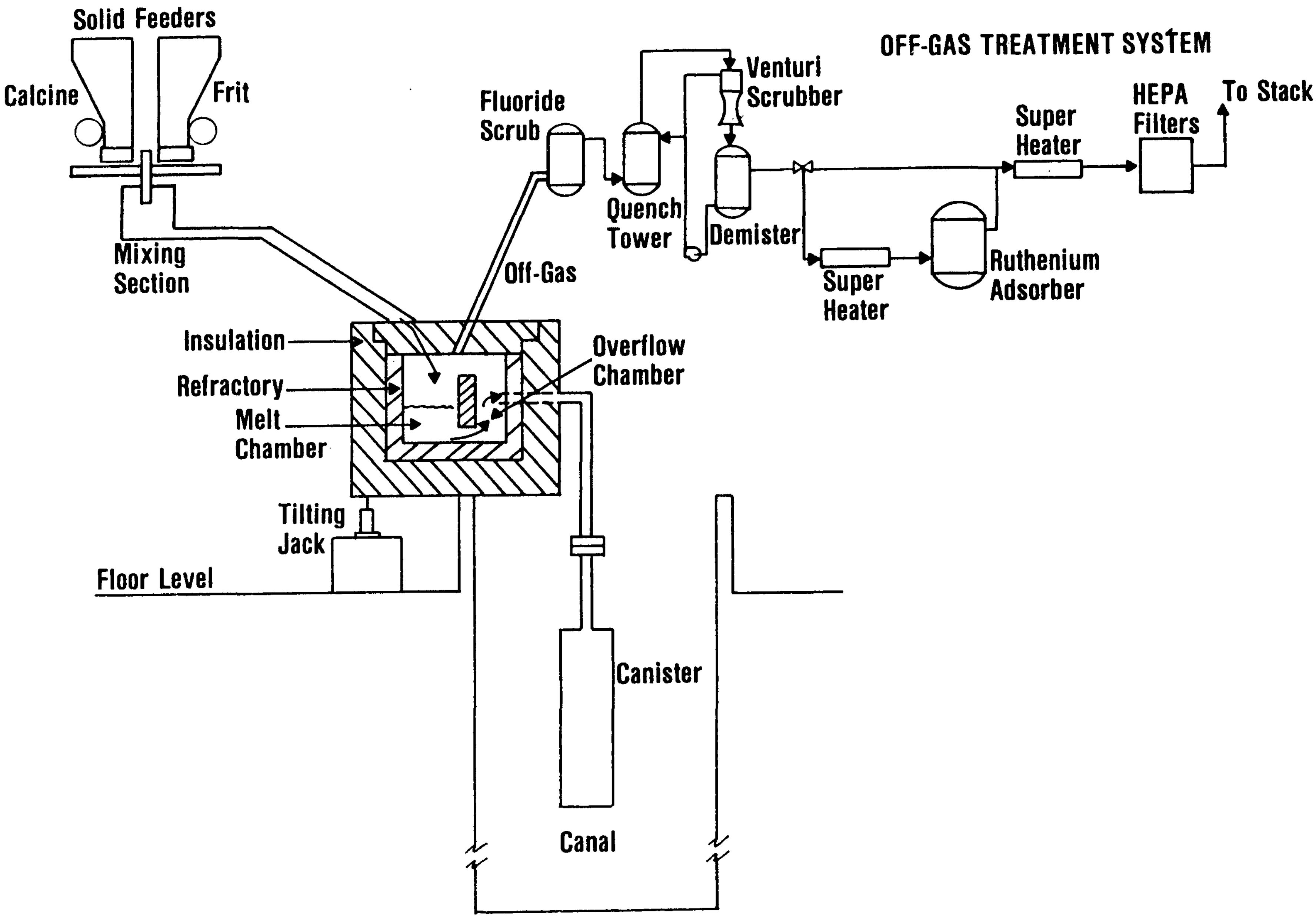

Figure 1. Conceptual Calcine Vitrification Process using a Continuous Joule-Heated Melter

III. Description of ICPP Wastes

Calcined wastes at the ICPP vary in composition as shown in Table I. Alumina calcine has not been processed since the late 1960's,[8] but a substantial amount of this waste (approximately 623 m^3) is presently stored in stainless steel bins at the ICPP.[9] The calcined waste may require special glass compositions for vitrification because of the high alumina content (about 89 wt%). There is also approximately 934 m^3 of zirconia calcine currently stored. Some physical properties of the zirconia calcine are shown in Table II. Less than 5% of the calcine would be from a stainless steel waste (electrolytic) with a high iron content. To vitrify this waste a modification in the glass flux or blending with the zirconia waste may be required. Sodium containing waste is presently stored as an acidic liquid waste (about 3.8 million litres). It is being calcined as a blend with zirconia waste ($\sim$3.5:1 zirconia to sodium waste) so the final calcine (Zr-Na) contains less than 5 percent sodium.

Table I

Calcined Waste Compositions

	Waste Type			
Composition (wt%)	Alumina	Zirconia	Zr-Na Blend	Electrolytic
Fe_2O_3				10-17
Al_2O_3	82-95	13-17	10-16	57-85
Na_2O	1-3		6-8	1.4-2.7
ZrO_2		21-27	16-19	
CaF_2		50-56	33-39	
Gd_2O_3				6-23
CaO		2-4	13-17	
NO_3	5-9	0.5-2	7-9.5	1-5
B_2O_3	0.5-2	3-4	2-3	2-6
Fission Product & Actinides	0.2-1	0.2-1	0.2-1	0.2-1
Miscellaneous	0.5-1.5	0.5-1.5	0.5-1.5	1-4

Table II

Properties of Fluidized-Bed Zirconia Calcine

Preparation Temperature, ^{o}C	400-550
Particle Size Bed, mm diameter	0.1-0.6
Fines, mm diameter	0.01-0.1
Density, g/cc	1.2-1.6
Nitrate Content, wt% (released between 500-750^{o}C)	1-3
Fission Product Content, %	0.2-1
Thermal Conductivity, W/m-^{o}K	0.2-0.28
Sintering Temperature, ^{o}C	>800
Major Leachable Elements	Cs, Sr, Cr

IV. Experimental and Analytical Methods

A. Glass Preparation

Experimental glasses were melted in 50 mL high-fired alumina crucibles. The crucibles contained a total of 30 grams of calcine and glass-forming additives when introduced to a furnace preheated to 1100°C. All glasses were made with simulated zirconia calcine prepared in a fluidized-bed calciner.[10] Three additions of 30, 25, and 20 grams each of the calcine-glass-forming mixture were made to the crucible at 30 minute intervals. Successive additions were smaller to prevent foaming over the top of the crucible as it filled. After the last addition, a 3-hour fining period (the time required to release evolved and entrained gases and to complete chemical dissolution) was used before pouring. The glass samples were then poured into graphite molds and transferred to an oven held at about 200°C, for slow cooling.

Upon pouring, the glasses were judged on a qualitative scale for viscosity. The scale ranged from readily pourable (similar to room temperature corn syrup) to highly viscous, or numerically 1 through 5, respectively. These ratings seem to be fairly constant and adequate for rapid comparison of many glass compositions.

B. Fluoride Content Analysis

Since ICPP calcine is high in fluoride content (23 wt%), fluoride volatility during melting has been an area of concern. Analysis of the glass for fluoride content has proved to be more practical than attempting to analyze the off-gas. Seven methods for determining fluoride content in glass have been compared (see Table III) and it is now believed that a dependable method has been found.[11] Potentiometric analysis appears to be in fair agreement with the colorimetric tests and with fluoride content expected in the glass. Potentiometric analysis is the easier and preferred of the two methods. Agreement of fluoride analysis between these two independent methods is the basis for assuming the analytical methods are accurate and dependable.

The potentiometric tests involve fusing about 0.5 g of the powdered glass (-16 mesh) sample with about 2 g NaOH in a nickel crucible, dissolving the fused mass in a solution of sodium citrate, triethylamine, and NaCl and then after dilution analyzing with a fluoride specific ion electrode. Fluoride is not lost during analysis, due to the extremely basic environment, and the test gives reproducible results. The pyrohydrolysis method involves heating about 1 g of the powdered glass with WO_3 and $Al(NO_3)_3$ at 900°C under moist air, driving off the fluoride which is then caught for analysis in a caustic bubbler system. This test has yielded rather low results, possibly caused by interference from other elements in the glass matrix. The colorimetric analysis uses either the solution from the potentiometric test or powdered glass. The solution or solid is heated in H_3PO_4 at 185°C to distill off the fluoride, which is again caught in a caustic bubbler for spectrophotometric measurement of fluoride using lanthanum-alizarin complexone. Results from this procedure confirm the results found with the potentiometric test, but the colorimetric analysis is far more time consuming. The nitric acid dissolution method consists of dissolving about 2 g of glass in 8 to 16 M HNO_3 at 80°C for 24 hours and then analyzing the solutions for fluoride. Although this test was performed on only one glass, it was time consuming and gave low results due to loss of off-gases and too many variable experimental parameters. X-ray fluorescence was also tried, but it produced poor results due to insufficient standards and the fact that fluoride is not well detected by this method. The weak fluoride signal produced is easily shadowed by the matrix effect of other constituents in the glass. Finally, the off-gas capture method consists of melting the glass raw materials and calcine in an ammonia-ammonium sulfate atmosphere and trapping the released fluorine as NaF in a caustic bubbler.[12] Results were inconsistent and there is some evidence that the ammonia atmosphere enhanced release of fluorine.

Table III

Comparison of Methods for Determining Fluoride Content in Glass

	Formulation No.			
	13	61	75	76
Method	Glass (wt% F^-)			
Potentiometric	5.5±.3	7.3±.3 7.1±.3	7.6±.3 7.2±.3	7.5±.3
Pyrohydrolysis	-	3.3±.1	3.6±.1	4.3±.1 3.4±.1
Colorimetric Solution	-	7.9±.4	7.2±.4	7.4±.4
Colorimetric Solids	-	5.9±.6 5.1±.6	6.8±.6 7.0±.6	7.9±.6 7.1±.6
Nitric Acid Dissolution	4.3±.6	-	-	-
X-Ray Fluorescence	Weak Signals and Interference from other Elements			
Off-Gas Capture	Inconsistent Results			
Calculated (based on calcine)	6.0±.4	7.7±.4	7.7±.4	7.7±.4

C. Leach Tests

The glasses were also compared for leach resistance. The leach tests are based on gross weight loss of the sample after a set length of time. A four gram sample of glass ground to between -16 and +30 mesh is rinsed with acetone, weighed, and placed in a 100 mL leachant solution at ambient temperature. After 19 hours on a magnetic stirrer, the solution and remaining sample are rinsed through a sintered glass filter with distilled water. After drying, the samples are weighed and a percent weight loss is calculated. There were five standard leachants used for this procedure. Three of the solutions were simulated groundwater brines, the fourth an NH_4-NH_4Cl solution buffered to a pH of 9.5, and the fifth a 1 M acetic acid solution buffered to a pH of between 3.6-3.8. Acid leaching showed the greatest differences in leach resistance and was therefore used for comparative leach rate measurements. It is the acid leach rates as weight percent lost over a 19 hour period that are referred to in this report.

The standard soxhlet leach test with constant reflux of distilled water at 95°C for 100 hours was also replaced by the acid leach test because measurements with the experimental glasses showed very little variation in leach resistance using the soxhlet method.

V. Glass Forming Additives Used

Silica (SiO_2) forms the basic tetrahedral structure in all of our glasses. Boric oxide (B_2O_3) a glass former in itself acts as a modifier when added to silica.[13] The B_2O_3 forms a planar structure which weakens the tetrahedral links thereby lowering the melting temperature and viscosity. The B_2O_3 should also improve the glass resistance to leaching and devitrification. Soda (Na_2O), the third major constituent in our glasses is simply a flux which breaks down the silica structure by interfering with the O:Si bonds to lower the viscosity of the glass. Soda also tends to make the glass more leachable.

Five minor additives were also evaluated to measure their effect on glass leach resistance and melt viscosity. Phosphorous pentoxide, a glass former, and the fluxes Li_2O, CaO, ZnO, and CuO were all added to the glasses in small amounts (<10 wt%) and various combinations (see Appendix A). These components were added as oxides, carbonates, $Na_2B_4O_7$-$5H_2O$ and Na_2SiO_3-$5H_2O$ to simulated zirconia calcine in a ratio of 2:1 (total glass forming components to calcine) on the basis of oxide weights alone.

From a bonding standpoint,[14] fluoride present in the calcine and copper present in the flux should act to decrease the viscosity of the glass, which was shown in the data taken. Also in agreement with bonding theory was the fact that Ca has little effect on the viscosity of the glass. On the contrary, the addition of Zr and P should have little effect on viscosity, but did indeed increase the viscosity of our waste glasses. The use of Li should increase the viscosity of a glass with a high O:Si ratio, whereas for the ICPP glasses the viscosity decreased even though the glasses have a high O:Si ratio. These contradictions may be due to the conflicting influences of the highly refractory ZrO_2 and Al_2O_3 with the fluxing action of the F^- which are all found in the calcine. The theoretical work referenced was conducted with widely varying but relatively simple glass compositions to assess individual additive effects on viscosity with no interference from other elements.

VI. Effects of Individual Glass-Forming Additives on Viscosity and Leach Resistance

Formulations were designed to combine with zirconia calcine to form a leach resistant low viscosity glass at about 1100°C. Compositions of 105 experimental glass fluxes used with zirconia calcine are shown in Appendix A. In addition, leach rates, relative viscosities, and waste loadings in the finished glasses are listed.

Effects of single glass additives were evaluated against leach rate and viscosity by varying each component individually in a flux which was mixed 2:1 with simulated zirconia calcine. All components were maintained at a constant concentration with the exception of silica which was varied to balance the changing component.

A. Effects of Na_2O Content

Table IV shows the range of sodium contents used. For a frit (Figure 2A) containing 2% CuO, 2% P_2O_5, 14% B_2O_3, and 12-24% Na_2O (balance is SiO_2), the acid leach rate and relative viscosity both apparently decrease steadily with increasing soda content. For a similar frit (Figure 2B), but without the P_2O_5, acid leach rates are higher than with the P_2O_5, but relative viscosities are drastically reduced at higher soda contents. Lowering the B_2O_3 content to 8% and leaving out the P_2O_5 in the original flux (Figure 2C) yields a glass with fairly constant leach resistance with varying Na_2O content. The viscosity curve still decreases steadily but at significantly higher soda contents.

B. Effects of B_2O_3 Content

In a glass using a flux matrix of 2% CuO, 2% P_2O_5, 16% Na_2O, and 10-18% B_2O_3 (again the balance made up by SiO_2), leach rates and relative viscosities (see Table V) both seem to increase with increasing borate content (Figure 3A). The same glass without the P_2O_5 and 24% Na_2O (Figure 3B) shows the same basic trend with borate content, but both the leach rates and viscosities are significantly lower. Finally, by increasing the soda content to 28%, still with no P_2O_5 present, the apparent trend breaks down (Figure 3C). Here as expected, the viscosities steadily decrease but the acid leach rates rapidly increase with higher B_2O_3 contents.

C. Effects of CuO Content

Small additions of CuO, (about 2-4%) seem to decrease leach rate while decreasing or leaving unchanged the viscosity of almost any matrix containing only one other minor constituent (i.e., CaO, Li_2O, P_2O_5, ZnO). Addition of CuO in most of the more complex matrices raises the leach rate and/or viscosity (Table VI). In a matrix of 16% soda, 14% borate, 2% phosphate, and 0-6% CuO, the typical effects of CuO may be seen (Figure 4). Though the viscosity is high due to the low soda content, both the viscosities and leach rates drop with addition of CuO until a 4% CuO content

Table IV

Effect of Na_2O Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%						
	SiO_2	Na_2O	B_2O_3	P_2O_5	CuO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
37	70	12	14	2	2	5	0.6
35	66	16	14	2	2	4	0.4
36	62	20	14	2	2	3	0.3
63	58	24	14	2	2	4	0.1
34	68	16	14	-	2	5	0.7
64	64	20	14	-	2	5	1
50	60	24	14	-	2	2	0.3
58	56	28	14	-	2	2	0.6
65	70	20	8	-	2	5	0.2
51	66	24	8	-	2	2	0.2
59	62	28	8	-	2	3	0.2

Table V

Effect of B_2O_3 Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%						
	SiO_2	Na_2O	B_2O_3	P_2O_5	CuO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
38	70	16	10	2	2	4	0.5
35	66	16	14	2	2	4	0.4
39	62	16	18	2	2	5	0.9
51	66	24	8	-	2	2	0.1
50	60	24	14	-	2	2	0.3
66	56	24	18	-	2	3	0.2
59	62	28	8	-	2	3	0.2
58	56	28	14	-	2	2	0.6
67	52	28	18	-	2	1	1.8

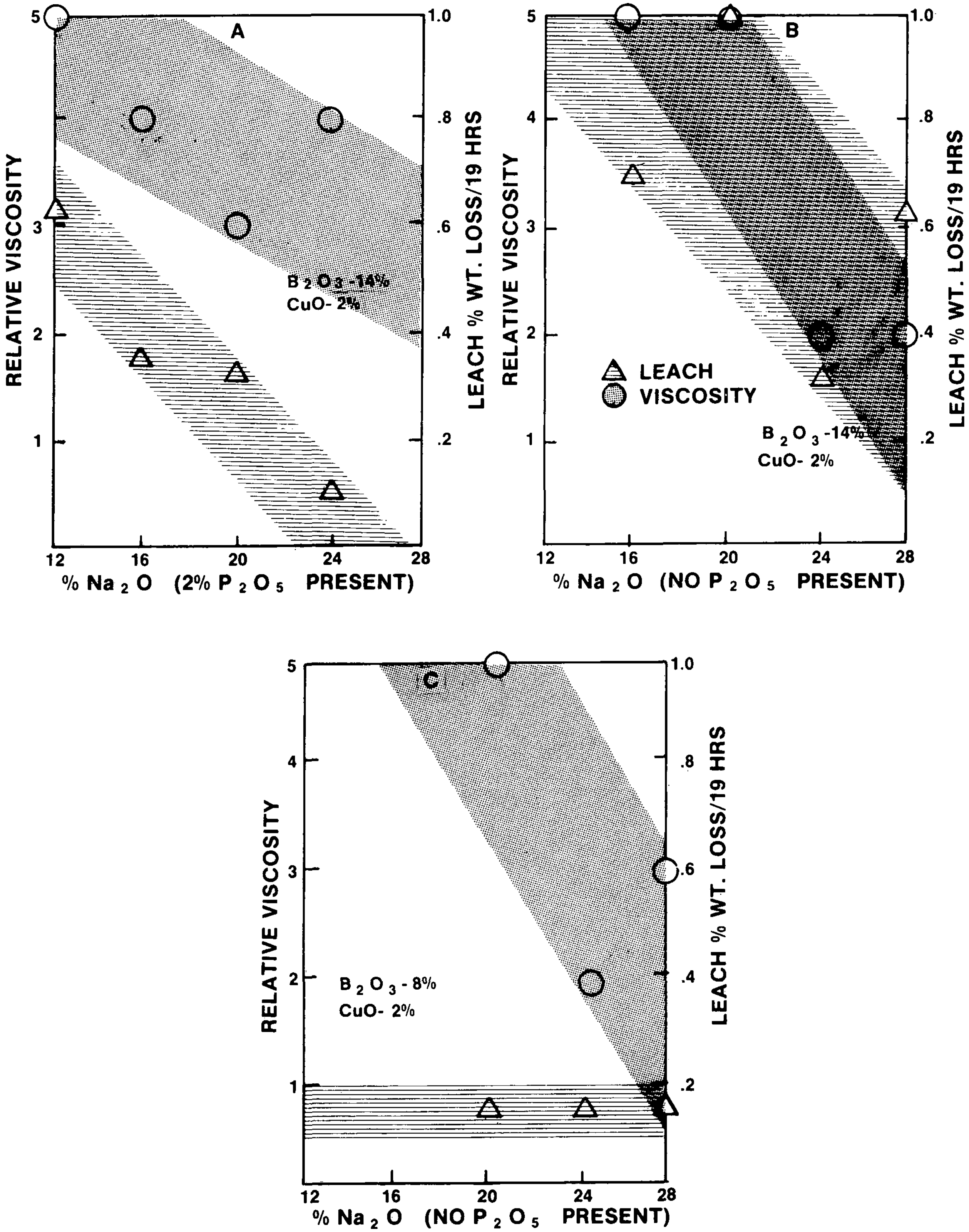

Figure 2. EFFECT OF Na_2O ON GLASS VISCOSITY AND ACID LEACH RATE

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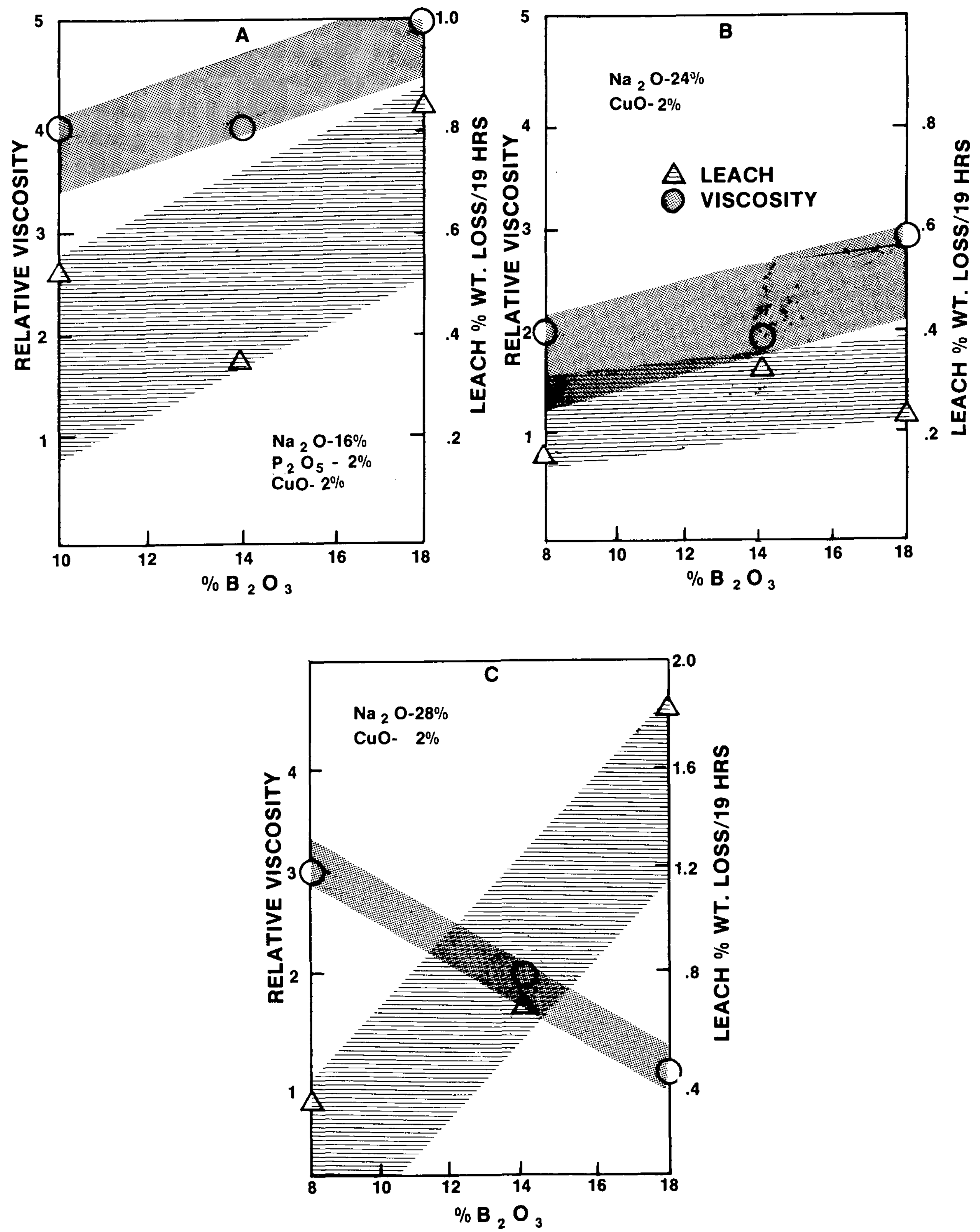

Figure 3. EFFECT OF B_2O_3 ON GLASS VISCOSITY AND ACID LEACH RATE

Table VI

Effect of CuO Content on Viscosity and Acid Leach Rate

of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
41	68	16	14	-	2	-	-	-	5	0.5
35	66	16	14	-	2	2	-	-	4	0.4
42	64	16	14	-	2	4	-	-	3	0.3
73	62	16	14	-	2	6	-	-	5	0.7
87	53	24	14	2	2	2	3	-	1	0.9
92	55	24	14	2	2	-	3	-	1	0.6
78	55	24	14	2	-	-	3	2	2	3
79	53	24	14	2	-	2	3	2	2	5
82	53	24	14	4	-	-	3	2	1	14
83	51	24	14	4	-	2	3	2	1	18
80	53	24	14	2	2	-	3	2	1	0.4
81	51	24	14	2	2	2	3	2	2	1
84	49	24	14	4	2	2	3	2	1	4
85	51	24	14	4	2	-	3	2	1	5
93	56	24	14	2	2	-	-	2	1	0.2
74	54	24	14	2	2	2	-	2	1	0.4
75	50	24	14	2	2	6	-	2	1	3
62	56	24	14	2	-	2	-	2	1	2
90	58	24	14	2	-	-	-	2	1	0.7
89	55	24	14	2	-	2	3	-	2	2
91	57	24	14	2	-	-	3	-	1	1
57	58	24	14	2	-	2	-	-	2	0.5
106	60	24	14	2	-	-	-	-	1	10
63	58	24	14	-	2	2	-	-	4	0.1
105	60	24	14	-	2	-	-	-	2	0.6
98	57	24	14	-	-	2	3	-	2	0.5
104	59	24	14	-	-	-	3	-	2	10
61	58	24	14	-	-	2	-	2	3	0.2
103	60	24	14	-	-	-	-	2	1	4
88	56	24	14	-	2	2	-	2	3	0.2
102	58	24	14	-	2	-	-	2	1	2
95	56	24	14	2	2	2	-	-	2	0.3
101	58	24	14	2	2	-	-	-	1	0.2
96	55	24	14	-	-	2	3	2	2	1
100	57	24	14	-	-	-	3	2	2	0.5
94	55	24	14	-	2	2	3	-	2	0.2
99	57	24	14	-	2	-	3	-	3	0.2
86	53	24	14	-	2	2	3	2	2	0.4
97	55	24	14	-	2	-	3	2	2	0.2
50	60	24	14	-	-	2	-	-	2	0.3
107	62	24	14	-	-	-	-	-	3	3

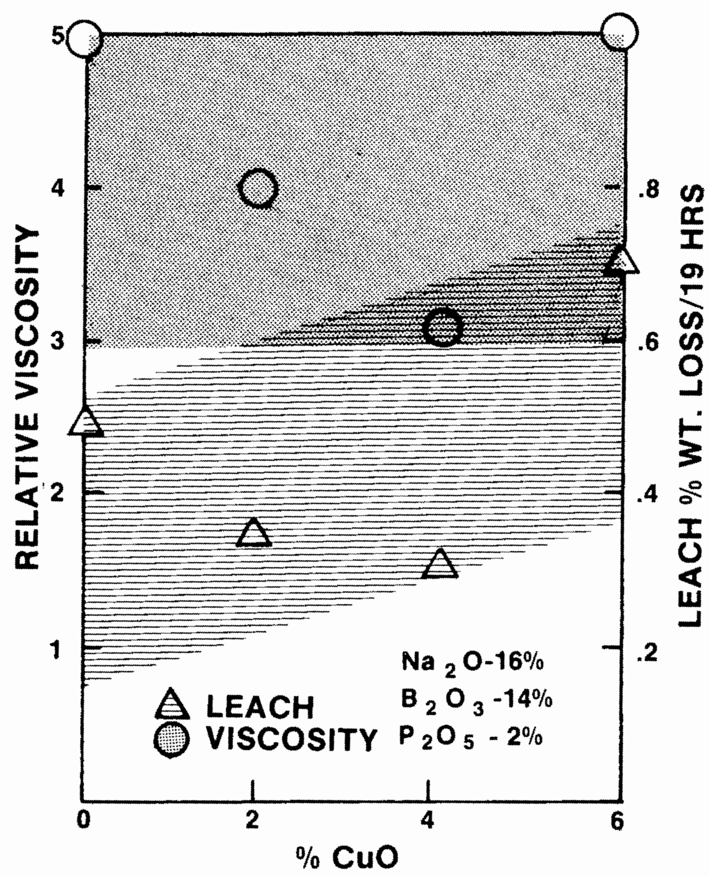

Figure 4. EFFECT OF CuO ON GLASS VISCOSITY AND ACID LEACH RATE

is reached. Above 4% CuO both viscosity and leach rate increase rapidly. As can be seen, the most favorable effects caused by CuO addition in terms of lowering the melting viscosity and acid leach rate are found in the simple glass formulations.

D. Effects of ZnO Content

In most cases the addition of ZnO above a concentration of 2 wt% seems to raise the viscosity and/or leach rate of the glass. Even at this level the benefits of ZnO addition are doubtful since the effect of decreasing leach rate is usually conflicting with an increase in viscosity (Figure 5, Table VII). Only in the matrix of 16% soda, 14% borate, and 2% cupric oxide (Figure 5A) does ZnO lower both the leach rate and viscosity. This effect is most favorable at a 2% ZnO content.

E. Effects of Li_2O Content

Additions of lithium oxide slowly decrease or leave unchanged melt viscosities, but drastically increase acid leach rates. In almost all cases (Table VIII, Figure 6) addition of even 2% Li_2O markedly increases the acid leach rate. Exceptions to this general rule are in the presence of P_2O_5 and for ZnO, or CaO alone without CuO present.

F. Effects of P_2O_5 Content

In most cases (Table IX) the addition of no more than 2% P_2O_5 is the most effective for producing low viscosity and low leach rates (Table IX). Addition of 2% phosphate usually decreases the acid leach rate, but additions greater than 2% tend to cause an increase in both viscosity and leach rate.

G. Effects of CaO Content

Addition of CaO seems to have little or no effect on the glass viscosity but almost always increases the acid leach rate (Table X). Exceptions are for additions made in the presence of Li_2O alone, P_2O_5 and ZnO, and ZnO alone, where leach rates are decreased with CaO. The effect of CaO is of particular interest since the calcined zirconia wastes contain about 30% calcium. The presence of about 10% calcium in the ICPP glasses may tend to make the glass more brittle by weakening the silica matrix, which may affect its storage characteristics, though this has yet to be verified.

Table VII

Effect of ZnO Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
34	68	16	14	-	-	2	-	-	4	0.7
53	66	16	14	-	-	2	-	2	3	0.1
54	64	16	14	-	-	2	-	4	3	0.2
56	62	16	14	-	-	2	-	6	5	0.4
51	66	24	8	-	-	2	-	-	2	0.1
55	64	24	8	-	-	2	-	2	3	0.3
69	62	24	8	-	-	2	-	4	3	0.3
110	60	24	8	-	-	2	-	6	2	3
50	60	24	14	-	-	2	-	-	2	0.3
61	58	24	14	-	-	2	-	2	3	0.2
70	56	24	14	-	-	2	-	4	2	0.5
108	54	24	14	-	-	2	-	6	1	10
57	58	24	14	2	-	2	-	-	2	0.5
62	56	24	14	2	-	2	-	2	1	2
72	54	24	14	2	-	2	-	4	1	3
109	52	24	14	2	-	2	-	6	1	17
95	56	24	14	2	2	2	-	-	2	0.3
74	54	24	14	2	2	2	-	2	1	0.4
76	50	24	14	2	2	2	-	6	1	2
87	53	24	14	2	2	2	3	-	1	0.9
81	51	24	14	2	2	2	3	2	1	1
89	55	24	14	2	-	2	3	-	2	2
79	53	24	14	2	-	2	3	2	2	5
78	55	24	14	2	-	-	3	2	2	3
91	57	24	14	2	-	-	3	-	1	1
88	56	24	14	-	2	2	-	2	3	0.1
83	58	24	14	-	2	2	-	-	4	0.1
92	55	24	14	2	2	-	3	-	2	0.6
80	53	24	14	2	2	-	3	2	1	0.4
94	55	24	14	-	2	2	3	-	2	0.2
86	53	24	14	-	2	2	3	2	2	0.4
106	60	24	14	2	-	-	-	-	1	10
90	58	24	14	2	-	-	-	2	2	0.7
101	58	24	14	2	2	-	-	-	1	0.3
93	56	24	14	2	2	-	-	2	2	0.2
98	57	24	14	-	-	2	3	2	2	0.5
96	55	24	14	-	-	2	3	2	2	1
99	57	24	14	-	2	-	3	-	3	0.2
97	55	24	14	-	2	-	3	2	2	0.2
104	59	24	14	-	-	-	3	-	2	10.8
100	57	24	14	-	-	-	3	2	2	0.5
105	59	24	14	-	2	-	-	-	2	0.6
102	58	24	14	-	2	-	-	2	1	2
107	62	24	14	-	-	-	-	-	3	3.9
103	60	24	14	-	-	-	-	2	1	4

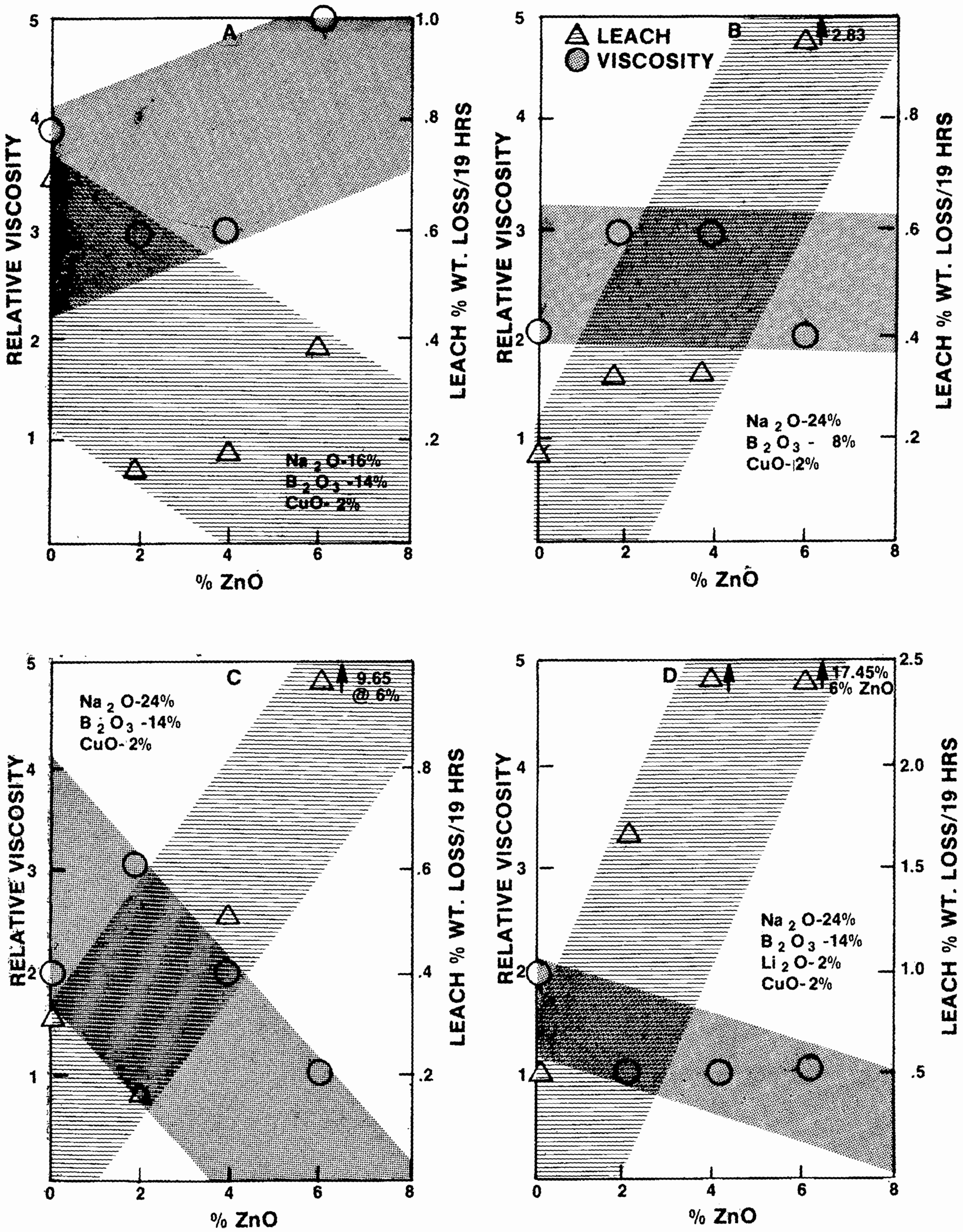

Figure 5. EFFECT OF ZnO ON GLASS VISCOSITY AND ACID LEACH RATE

Table VIII

Effect of Li_2O Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
50	60	24	14	-	-	2	-	-	2	0.3
57	58	24	14	2	-	2	-	-	2	0.5
60	56	24	14	4	-	2	-	-	2	2
61	58	24	14	-	-	2	-	2	3	0.2
62	56	24	14	2	-	2	-	2	1	2
71	54	24	14	4	-	2	-	2	1	8
47	62	16	14	2	2	2	-	2	3	0.3
49	60	15.5	13.5	5	2	2	-	2	1	2
100	57	24	14	-	-	-	3	2	2	0.5
78	55	24	14	2	-	-	3	2	2	3
82	53	24	14	4	-	-	3	2	1	14
79	53	24	14	2	-	2	3	2	2	5
83	51	24	14	4	-	2	3	2	1	18
86	53	24	14	-	2	2	3	2	2	0.4
81	51	24	14	2	2	2	3	2	2	1
84	49	24	14	4	2	2	3	2	1	4
88	56	24	14	-	2	2	-	2	3	0.2
74	54	24	14	2	2	2	-	2	1	0.4
99	57	24	14	-	2	-	3	-	3	0.2
92	55	24	14	2	2	-	3	-	1	0.6
1-2	58	24	14	-	2	-	-	2	1	2
93	56	24	14	2	2	-	-	2	2	0.2
94	55	24	14	-	2	2	3	-	2	0.2
87	53	24	14	2	2	2	3	-	1	0.9
70	56	24	14	-	-	2	-	4	2	0.5
72	54	24	14	2	-	2	-	4	1	3
105	60	24	14	-	2	-	-	-	2	0.6
101	58	24	14	2	2	-	-	-	1	0.3
96	55	24	14	-	-	2	3	2	2	1
79	53	24	14	2	-	2	3	2	2	5
83	51	24	14	4	-	2	3	2	1	18
97	55	24	14	-	2	-	3	2	2	0.1
80	53	24	14	2	2	-	3	2	1	0.4
85	51	24	14	4	2	-	3	2	1	5
103	60	24	14	-	-	-	-	2	-	4
90	58	24	14	2	-	-	-	2	2	0.7
104	59	24	14	-	-	-	3	-	2	10
91	57	24	14	2	-	-	3	-	2	1
63	58	24	14	-	2	2	-	-	4	0.1
95	56	24	14	2	2	2	-	-	2	0.3
98	57	24	14	-	-	2	3	-	2	0.5
89	55	24	14	2	-	2	3	-	2	2
107	62	24	14	-	-	-	-	-	3	3
106	60	24	14	2	-	-	-	-	1	10
108	54	24	14	-	-	2	-	6	1	10
109	52	24	14	2	-	2	-	6	1	17

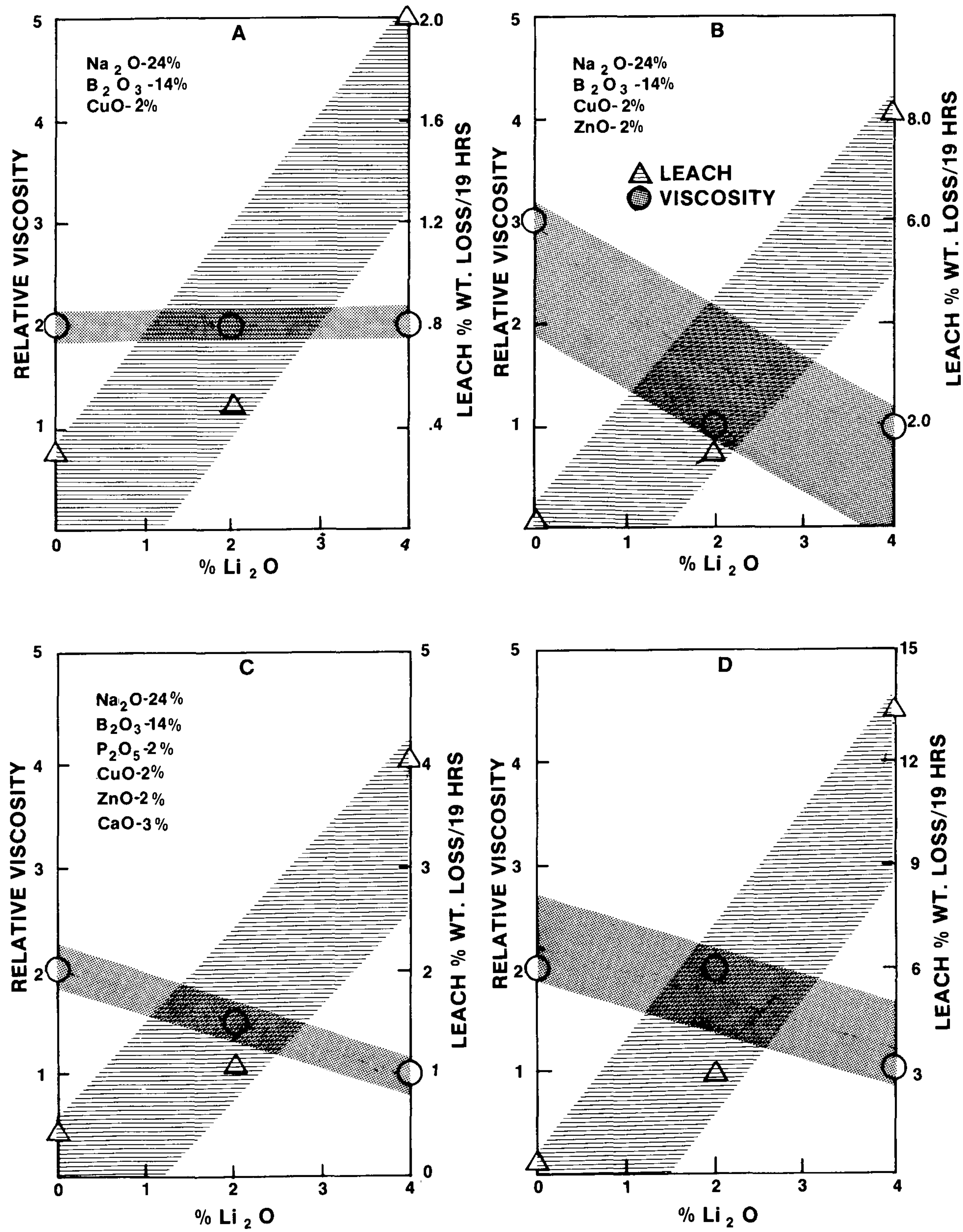

Figure 6. EFFECT OF Li_2O ON GLASS VISCOSITY AND ACID LEACH RATE

Table IX

Effect of P_2O_5 Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
34	68	16	14	-	-	2	-	-	3	0.7
35	66	16	14	-	2	2	-	-	4	0.4
40	64	16	14	-	4	2	-	-	5	0.8
50	60	24	14	-	-	2	-	-	2	0.3
63	58	24	14	-	2	2	-	-	4	0.1
68	56	24	14	-	4	2	-	-	5+	1
78	55	24	14	2	-	-	3	2	2	3
80	53	24	14	2	2	-	3	2	1	0.4
83	51	24	14	4	-	2	3	2	1	18
84	49	24	14	4	2	-	3	2	1	4
79	53	24	14	2	-	2	3	2	2	5
81	55	24	14	2	2	2	3	2	2	1
62	56	24	14	2	-	2	-	2	1	2
74	54	24	14	2	2	2	-	2	1	0.4
87	53	24	14	2	2	2	3	-	1	0.9
89	55	24	14	2	-	2	3	-	2	2
82	53	24	14	4	-	-	3	2	1	14
85	51	24	14	4	2	-	3	2	1	5
61	58	24	14	-	-	2	-	2	3	0.2
88	56	24	14	-	2	2	-	2	3	0.2
107	62	24	14	-	-	-	-	-	3	3
105	60	24	14	-	2	-	-	-	2	0.6
96	55	24	14	-	-	2	3	2	2	1
86	53	24	14	-	2	2	3	2	2	0.4
90	58	24	14	2	-	-	-	2	2	0.7
93	56	24	14	2	2	-	-	2	2	0.2
91	57	24	14	2	-	-	3	-	2	1
92	55	24	14	2	2	-	3	-	2	0.6
98	57	24	14	-	-	2	3	-	2	0.5
94	55	24	14	-	2	2	3	-	2	0.2
57	58	24	14	2	-	2	-	-	2	0.5
95	-	24	14	2	2	2	-	-	2	0.3
100	57	24	14	-	-	-	3	2	2	0.2
97	55	24	14	-	2	-	3	2	2	0.5
106	60	24	14	2	-	-	-	-	1	10
101	58	24	14	2	2	-	-	-	1	0.3
103	60	24	14	-	-	-	-	2	1	4
102	58	24	14	-	2	-	-	2	1	2

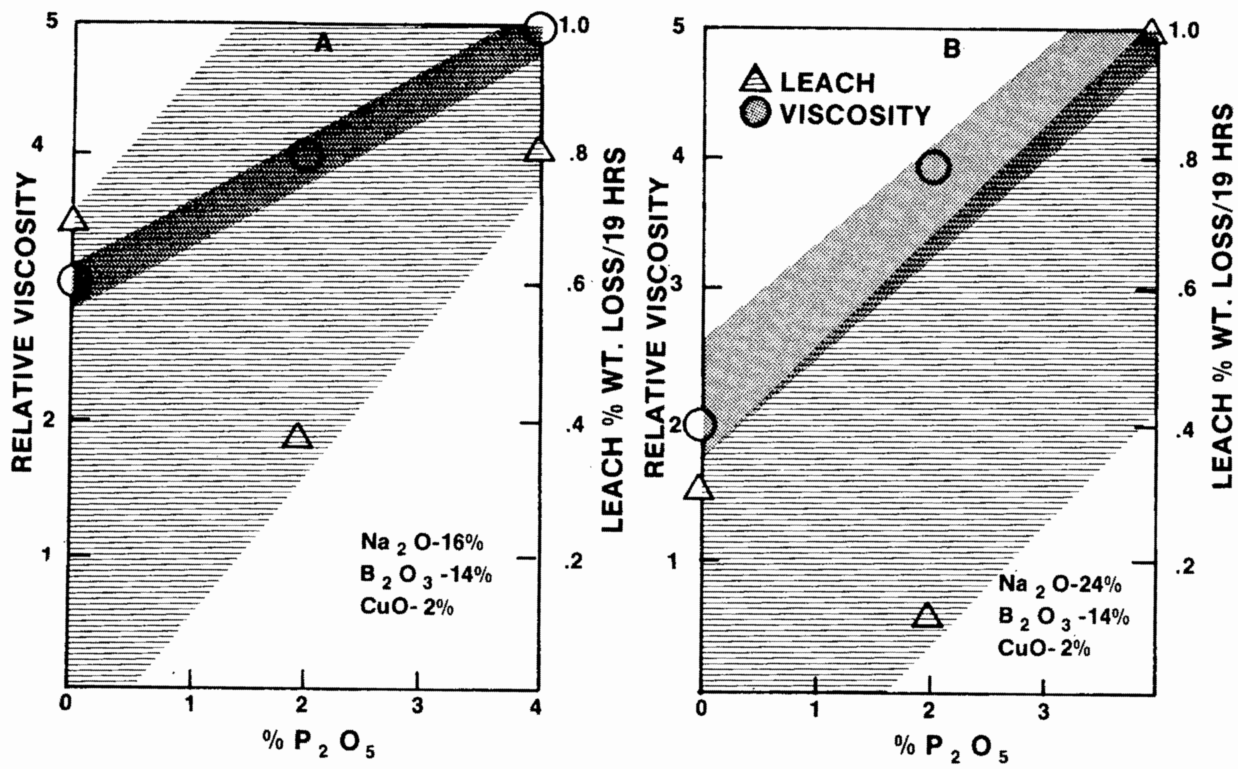

Figure 7. EFFECT OF P_2O_5 ON GLASS VISCOSITY AND ACID LEACH RATE

Table X

Effect of CaO Content on Viscosity and Acid Leach Rate of a Glass Containing 33 wt% ZrO Calcine

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
62	56	24	14	2	-	2	-	2	1	2
79	53	24	14	2	-	2	3	2	2	5
74	54	24	14	2	2	2	-	2	1	0.4
81	51	24	14	2	2	2	3	2	2	1
71	54	24	14	4	-	2	-	2	1	8
83	51	24	14	4	-	2	3	2	1	18
90	58	24	14	2	-	-	-	2	2	0.7
78	55	24	14	2	-	-	3	2	2	3
57	58	24	14	2	-	2	-	-	1	2
89	55	24	14	2	-	2	2	-	2	2
86	53	24	14	-	2	2	3	2	2	0.3
88	56	24	14	-	2	2	-	2	2	0.2
101	58	24	14	2	2	-	-	-	1	0.3
92	55	24	14	2	2	-	3	-	2	0.6
80	53	24	14	2	2	-	3	2	1	0.4
93	56	24	14	2	2	-	-	2	1	0.2
95	56	24	14	2	2	2	-	-	2	0.3
87	53	24	14	2	2	2	3	-	1	0.9
106	60	24	14	2	-	-	-	-	1	10
91	57	24	14	2	-	-	3	-	2	1
101	58	24	14	2	2	-	-	-	1	0.3
92	55	24	14	2	2	-	3	-	2	0.6
63	58	24	14	-	2	2	-	-	4	0.1
94	55	24	14	-	2	2	3	-	2	0.2
61	58	24	14	-	-	2	-	2	3	0.2
96	55	24	14	-	-	2	3	2	2	1
102	58	24	14	-	2	-	-	2	1	2
97	55	24	14	-	2	-	3	2	2	0.2
50	60	24	14	-	-	2	-	-	2	0.3
98	57	24	14	-	-	2	3	-	2	0.5
105	60	24	14	-	2	-	-	-	2	0.6
99	57	24	14	-	2	-	3	-	3	0.2
103	60	24	14	-	-	-	-	2	1	4
100	58	24	14	-	-	-	3	2	2	0.5
107	62	24	14	-	-	-	-	-	3	3
104	59	24	14	-	-	-	3	-	2	10

VII. Effects of Varying Minor Additive Combinations on Glass Viscosity and Leach Resistance

To gain knowledge about the general effects of varying combinations of minor components on viscosity and leach rate at a fixed temperature, a single base matrix was chosen and all combinations of the minor additives were tested. As can be seen in the foregoing discussion, the best glasses based on low viscosity and leach rate contained 24% Na_2O and 14% B_2O_3, so these Na_2O and B_2O_3 concentrations were chosen as the base matrix. The concentration of the additives appeared to be most effective at decreasing viscosity at 2%, with the exception of 3% for CaO as shown in the previous section, so the additives were used at these concentrations. The additives were taken one at a time, then 2, 3, 4, and finally all 5 in one glass (Table XI). Glasses with relative viscosities of less than 3 and acid leach rates below 1.0 wt% loss in 19 hours were considered acceptable as candidates for use as waste glasses.

Statistical analyses on the data for precision and accuracy showed that leach rates had to differ by a factor of at least 2.7 to be significantly different due to the variations observed in the leach tests. The analyses also showed that to produce a leach-resistant, low-viscosity glass containing only a single additive, CuO was the best; for two additives it is best to take CuO or P_2O_5 with CaO or ZnO or Li_2O, excluding P_2O_5 and ZnO together. For three additives the best combinations were P_2O_5 and any two others. Use of phosphate generally gave a more leach resistant glass. Based on these results and the viscosity and leach rate limitations stated above, glasses 50, 86, 94, and 95 were chosen for further testing.

The crucibles, crushed samples, and poured buttons were saved from almost all of the experimental glasses. In addition to viscosity and leach rate comparisons, these melts were compared qualitatively for homogeneity, smoothness, and porosity in both crucibles and buttons, and glasses 51, 66, and 101 were also chosen for further testing. Glasses 51 and 66 were not of the 24% Na_2O, 14% B_2O_3 type, but had favorable appearances and set upper and lower bounds on borate content. Both glasses contain CuO as the only minor constituent as does frit No. 50, and both contain 24% Na_2O, but frit 51 has only an 8% borate content whereas glass 66 contains 18% borate. Although low borate in frit 51 and the low silica in frit 66 (56%) may produce a glass susceptible to devitrification, they were chosen as lower and upper bounds for practical borate content for comparitive purposes. Glass 101 was chosen for its very low viscosity and leach rate even though it contained Li_2O and P_2O_5.

These seven frits were then made up and added to simulated zirconia calcine in frit to calcine ratios of 3:1, 2:1, and 3:2. This would yield glasses having waste loadings of 25, 33, and 40% by weight. Glasses 51, 66, and 101 with each of the three waste loadings were then melted at temperatures of 1050, 1100, and 1200^oC for 3 hours giving 9 different samples of each glass. Acid leach tests on ground samples and relative melt viscosities are shown in Table XII. In general, leach resistance decreased while viscosities were virtually unaffected with increasing temperatures. Since the 1200^oC melting temperature had no beneficial effect, glasses 50, 86, 94, and 95 were made with all three waste loadings but at 1100^oC only.

Table XI

Effects of Minor Glass Constituents on

Viscosity and Acid Leach Rate of a Glass Containing

33 wt% ZrO Calcine, 24% Na_2O, 14% B_2O_3

Formulation Number	Frit Composition, wt%							
	SiO_2	Li_2O	P_2O_5	CuO	CaO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
50	60	-	-	2	-	-	2	0.3
105	60	-	2	-	-	-	2	0.6
107	62	-	-	-	-	-	3	3
103	60	-	-	-	-	2	1	4
104	59	-	-	-	3	-	2	10
106	60	2	-	-	-	-	1	10
63	58	-	2	2	-	-	4	0.1
61	58	-	-	2	-	2	3	0.2
99	57	-	2	-	3	-	3	0.2
101	58	2	2	-	-	-	1	0.3
57	58	2	-	2	-	-	2	0.4
98	57	-	-	2	3	-	2	0.5
100	57	-	-	-	3	2	2	0.5
90	58	2	-	-	-	2	2	0.7
91	57	2	-	-	3	-	1	1
102	58	-	2	-	-	2	1	2
93	56	2	2	-	-	2	1	0.2
94	55	-	2	2	3	-	2	0.2
97	55	-	2	-	3	2	2	0.2
95	56	2	2	2	-	-	2	0.3
92	55	2	2	-	3	-	1	0.6
96	55	-	-	2	3	2	2	1
88	56	-	2	2	-	2	2	1
62	56	2	-	2	-	2	1	2
89	55	2	-	2	3	-	2	2
78	55	2	-	-	3	2	2	3
80	53	2	2	-	3	2	1	0.4
74	54	2	2	2	-	2	1	0.4
86	53	-	2	2	3	2	2	0.4
87	53	2	2	2	3	-	1	0.9
81	51	2	2	2	3	2	2	1
79	53	2	-	2	3	2	2	5

Table XII

Effects of Melt Temperature and Calcine Loading on Acid Leach Rate and Melt Viscosity for Glass No. 51*

		Melt Temperature, °C					
		1050		1100		1200	
Calcine Content wt%	Formulation Number	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
25	51	2	2	2	0.7	3	2
	101	2	4	1	3	1	2
	95			1	7		
	86			1	8		
	94			1	8		
	50			1	11		
	66	1	15	1	17	1	16
33	51	1	0.3	2	0.2	2	1
	101	2	0.9	1	0.3	2	5
	50			1	4		
	86			1	5		
	94			1	5		
	95			1	5		
	66	2	8	3	11	1	11
40	51	5	4	2	1	1	2
	101	2	1	1	3	1	7
	50			1	4		
	95			1	6		
	86			1	7		
	94			1	7		
	66	2	7	1	9	1	11

* Data presented experimentally determined independent from that in the rest of the text.

Increasing leach rates with melt temperature may be due to dissolution of the crystalline CaF_2 phase leaving compounds in a more leachable amorphous form. Viscosities and acid leach rates for these glasses are also shown in Table XII.

Only glass 51 maintained a uniform leach resistance even at high melt temperatures and 40% waste loading. Based on these findings, glass 51 with 33% ZrO calcine was chosen for more extensive testing. Cesium leach rate for this glass was found to be 1.8% of the total Cs in a soxhlet extractor after 11 days at 95°C. Further testing was done on glass 51 to determine its ability to incorporate dolomite (a calciner startup material) and alumina calcine in a glass normally containing 33% zirconia calcine, up to 10% of the calcine was replaced with dolomite without significantly increasing the acid leach rate or viscosity. Substituting alumina calcine for up to 15% of the zirconia calcine fraction also did not increase the leach rate or viscosity notably. Using alumina calcine for 20 to 50% of the waste fraction increased the leach rate between 4 and 7 fold and increased the viscosity on the relative scale from 1 to 4 or 5. These results indicate that glass flux 51 will indeed produce a satisfactory glass with broad variations in the calcine composition.

VIII. Glass Melting Characteristics

Physical properties of tested glasses are shown in Appendix B. The mixture of glass flux and calcine sinters at 600°C compared to the calcine sintering temperature of 800°C. As the calcine-flux mixture melts, nitrates, CO_2, H_2O, and some fluorides are volatilized. These gases produce only minor foaming at 1100°C and may even help to fine the glass by increasing the mixing. The broad particle size distribution of the calcine may increase the glass fining time by controlling the diffusion rate of reactants in particles of varying size.

Fluoride is of major concern for its potential corrosive nature on electrodes, refractories, and in the off-gas. The potentiometric method was used to determine the fluoride content in glass 51 over 3 melt temperatures with 3 waste loadings; the results are shown in Table XIII. Fluoride volatility (wt% lost) becomes more severe at higher temperatures, but seems to be unaffected by varying the calcine loading. The fluoride is probably held in the glass fairly well due to the caustic nature of the flux. Finally, the thermal conductivity of the calcine is only 30 to 50% (0.2-0.28 vs. .43-.74 W/m-K) of that of the finished glass which may help in providing a cold cap (an unmelted layer) on top of the glass melt to keep down volatility of fluorides.

Table XIII

Effects of Melt Temperature and Calcine Loading on Glass 51 Fluoride Content

Calcine, wt%	Fluoride Content In Glass	Melt Temperature, °C 1050	1100	1200
25	wt% F^-	4.9	4.9	4
	(% F^- lost)	(15)	(15)	(30)
33	wt% F^-	6.9	6.2	8.7
	(% F^- lost)	(10)	(19)	(5.4)
40	wt% F^-	8.2	8.7	6.7
	(% F^- lost)	(11)	(5.4)	(27)

IX. Devitrification Effects

Short term devitrification tests were done on glasses 101 and 51. Samples were maintained at 700 and 800°C. Crystalline analysis and both acid and soxhlet leach tests were done on both glasses as poured, and after 24 hours, 2 weeks, and 60 days of devitrification (see Tables XIV, XV).

The major crystalline phase detected was CaF_2 ranging from 10 to 12 wt% in the as-poured samples. The only other crystalline material found was trace amounts of Hiortdahlite $((Na,Ca,RE,Y)_3\ Zr_{1-x}\ (Si_2O_7)(F,OH,O)_2)$. After devitrification the crystalline CaF_2 content was lower or about the same as the original glass. The CaF_2 apparently dissolves slowly into the glass at these temperatures.

Acid leach rates tend to increase with decreasing crystalline CaF_2 content and storage time at 700 to 800°C. This would indicate that perhaps the breakdown of CaF_2 crystals leaves the matrix more open to acid attack. Soxhlet leach rates though, do not appear to change with elevated temperature storage time.

Table XIV

Crystalline CaF_2 Content (wt%) in

Glasses 51 and 101 Containing 33 wt% ZrO Calcine,

Before and After Devitrification

		700° Treatment			800°C Treatment		
Glass No.	As Poured	24 hr	2 wk	60 d	24 hr	2 wk	60 d
51	10	12	12	9.6	10	6	7.2
101	12	10	8	7.6	8	6	3.2

Table XV

Leach Rates of Glasses No. 51 and 101

Containing 33 wt% ZrO_2 Calcine,

Before and After Devitrification

Formulation Number	Devitrification Time, days	Devitrification Temp, °C	Acid Leach Rate, wt% Lost/19 hr	Soxhlet Leach (11 days) Cs* wt% Lost	Cs* $g/cm^2/d \times 10^5$	Sr* wt% Lost	Sr* $g/cm^2/d \times 10^5$	Total wt% Lost	Total $g/cm^2/d \times 10^5$
51	0	—	0.7	11	25	4.9	12	3.5	8.4
	1	700	0.9	5.6	13	2.5	5.9	2.8	6.7
	1	800	1.5	10	24	4.1	9.7	4.8	11
	14	800	3.2	4.2	9.9	3.0	7.0	3.5	8.3
	60	700	2.5	—	—	8.3	20	2.2	5.3
	60	800	—	—	—	2.1	5.0	4.0	9.4
101	0	—	2.4	5.8	14	4.7	11	9.5	22
	1	700	7.1	14	33	1.3	3.0	6.1	14
	1	800	7.8	11	26	2.2	5.2	4.7	11
	14	800	14	6.5	15	2.5	5.9	5.6	13
	60	700	18	—	—	3.4	8.0	8.2	19
	60	800	20	—	—	6.5	15	7.4	17

*Calculations based on a measured amount of Cs and Sr in the calcine.

X. Conclusions and Recommendations

Based upon the original criteria of designing a flux which would combine with zirconia calcine to form a leach resistant, low viscosity glass at 1100°C, glass 51 seems to be the best candidate to date. In addition to these qualifications, glass 51 appears to be flexible enough to incorporate large variations of alumina as well as dolomite substitutions for zirconia calcine.

Viscosity data are not absolute numbers in this report but serve satisfactorily for comparison of one glass to another. This data does indicate, however, that the simple glass formulations tested to date are at least as good as, if not better than, the more complex matrices for producing leach resistant and low viscosity glasses with zirconia calcine.

Further testing of the glass for effects on leach resistance due to devitrification and the effects of Fe_2O_3 on viscosity and leach rate need to be measured. Any influence on the glass of alkalies mixed on an equimolar basis and added to the frit will also be assessed. Activation analysis should be used to better determine the extent of individual element leaching.

Modifications of the flux used to produce a glass with zirconia calcine or a new flux will probably be needed to treat the previously mentioned sodium, aluminum, electrolytic, and stainless steel wastes.

XI. References

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APPENDIX A

APPENDIX A

Experimental Glass Formulations

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CaO	CuO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
1	-	-	-	-	-	-	-	-	-	7
7	-	-	-	-	-	-	-	-	-	0.6
8	-	-	-	-	-	-	-	-	-	2
9	-	-	-	-	-	-	-	-	-	0.8
10	-	-	-	-	-	-	-	-	-	21
11	-	-	-	-	-	-	-	-	-	2
12	50.1	26.9	16.2	1.7	3.4	-	-	1.7	-	2
13	51.8	28.3	12.9	2.1	-	2.8	-	2.1	1	32
14	59.4	21.7	11.2	2.3	-	3.1	-	2.3	2	23
15	61.1	14.6	15.7	2.6	-	3.4	-	2.6	1	9
16	55.1	25.6	11.9	2.2	-	2.9	-	2.2	1	25
17	62.5	20.6	9.2	2.3	-	3.1	-	2.3	1	11
18	51.3	19.2	21.4	2.4	-	3.3	-	2.4	2	36
19	56.9	20.7	14.4	2.4	-	3.2	-	2.4	2	32
20	53.4	26.0	23.3	2.2	-	2.9	-	2.2	2	11
21	50.4	30.5	12.4	2.0	-	2.7	-	2.0	-	60
22	47.8	34.3	11.6	1.9	-	2.5	-	1.9	2	50
23	67.6	6.2	16.6	2.9	-	3.8	-	2.9	-	4
24	51.8	28.3	12.9	2.1	2.8	-	-	2.1	2	18
25	47.8	34.3	11.6	1.9	2.5	-	-	1.9	2	32
26	60.7	16.9	14.9	4.7	2.8	-	-	-	-	3
26A	60.7	16.9	14.9	4.7	2.8	-	-	-	-	2
27	52.9	22.0	13.7	6.9	2.6	-	1.9	-	1	63
28	61.0	14.6	15.8	2.6	3.4	-	-	2.6	4	1
29	56.7	20.8	14.5	2.4	3.2	-	-	2.4	3	0.3
30	62.7	14.6	15.8	2.6	1.7	-	-	2.6	5	0.1
31	51.0	18.2	25.2	2.1	1.4	-	-	2.1	4	0.1
32	53.6	26.3	14.0	2.3	1.5	-	-	2.3	2	71
33	53.4	26.0	13.4	4.0	2.6	-	1.8	-	2	20
34	68.0	16.0	14.0	-	-	-	2.0	-	4	0.7
35	66.0	26.0	14.0	-	2.0	-	2.0	-	4	0.4
36	62.0	20.0	14.0	-	2.0	-	2.0	-	3	0.3
37	70.0	12.0	14.0	-	2.0	-	2.0	-	5	0.6
38	70.0	16.0	10.0	-	2.0	-	2.0	-	4	0.5
39	62.0	16.0	18.0	-	2.0	-	2.0	-	5	0.9
40	64.0	16.0	14.0	-	4.0	-	2.0	-	5	0.8
41	61.0	16.0	14.0	-	2.0	-	2.0	-	5	0.5
42	64.0	16.0	14.0	-	2.0	-	4.0	-	3	0.3
43	60.0	20.0	10.0	4.0	2.0	-	4.0	-	2	3
44	56.7	20.8	14.5	2.4	3.2	-	2.4	-	2	2
45	56.7	20.8	14.5	2.4	3.2	-	-	2.4	1	1
46	60	22.0	8.0	4.0	2.0	-	4	-	1	6
47	62	16.0	14.0	2.0	2.0	-	2	2	3	0.3
48	57	19.0	16.0	2.5	1.5	-	2	2	2	4
49	60	15.5	13.5	5.0	2.0	-	2	2	1	2
50	60	24	14	-	-	-	2	-	2	0.3

APPENDIX A

Experimental Glass Formulations
(continued)

Formulation Number	Frit Composition, wt% SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CaO	CuO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
51	66	24	8	-	-	-	2	-	2	0.2
52	65	24	8	-	1	-	2	-	3	0.2
53	66	16	14	-	-	-	2	2	4	0.1
54	64	16	14	-	-	-	2	4	3	0.2
55	64	24	8	-	-	-	2	2	3	0.3
56	62	16	14	-	-	-	2	6	5	0.4
57	58	24	14	2	-	-	2	-	2	0.4
58	56	28	14	-	-	-	2	-	3	0.6
59	62	28	8	-	-	-	2	-	3	0.2
60	56	24	14	4	-	-	2	-	2	2
61	58	24	14	-	-	-	2	2	3	0.2
62	56	24	14	2		-	2	2	1	2
63	58	24	14	-	2	-	2	-	4	0.1
64	64	20	13	-	-	-	2	-	5	1
65	70	20	8	-	-	-	2	-	5	0.2
66	56	24	18	-	-	-	2	-	3	0.2
67	52	28	18	-	-	-	2	-	1	2
68	56	24	14	-	4	-	2	-	5	1
69	62	24	8	-	-	-	2	4	3	0.3
70	56	24	14	-	-	-	2	4	2	1
71	54	24	14	4	-	-	2	2	1	8
72	54	24	14	2	-	-	2	4	1	3
73	62	16	14	-	2	-	6	-	5	0.7
74	64	24	14	2	2	-	2	2	1	0.4
75	80	24	14	2	2	-	6	2	1	3
76	50	24	14	2	2	-	2	6	1	2
77	50	28	14	2	2	-	2	2	1	3
78	55	24	14	2	-	3	-	2	2	3
79	53	24	14	2	-	3	2	2	2	5
80	53	24	14	2	2	3	-	2	1	0.4
81	51	24	14	2	2	3	2	2	2	1
82	53	24	14	4	-	3	-	2	1	14
83	51	24	14	4	-	3	2	2	1	18
84	49	24	14	4	2	3	2	2	1	4
85	51	24	14	4	2	3	-	2	1	5
86	53	24	14	-	2	3	2	2	2	0.4
87	53	24	14	2	2	3	2	-	1	0.9
88	56	24	14	-	2	-	2	2	3	0.2
89	55	24	14	2	-	3	2	-	2	2
90	58	24	14	2	-	-	-	2	2	0.7
91	57	24	14	2	-	3	-	-	2	1
92	55	24	14	2	2	3	-	-	2	0.6
93	56	24	14	2	2	-	-	2	2	0.2
94	55	24	14	-	2	3	2	-	2	0.2
95	56	24	14	2	2	-	2	-	2	0.3
96	55	24	14	-	-	3	2	2	2	1
97	55	24	14	-	2	3	-	2	2	0.2
98	57	24	14	-	-	3	2	-	2	0.5
99	57	24	14	-	2	3	-	-	3	0.2
100	57	24	14	-	-	3	-	2	2	0.5

APPENDIX A

Experimental Glass Formulations
(continued)

Formulation Number	Frit Composition, wt%									
	SiO_2	Na_2O	B_2O_3	Li_2O	P_2O_5	CaO	CuO	ZnO	Relative Viscosity	Acid Leach Rate, wt% Lost/19 hr
101	58	24	14	2	2	-	-	-	2	0.3
102	58	24	14	-	2	-	-	2	1	2
103	60	24	14	-	-	-	-	2	1	4
104	59	24	14	-	-	3	-	-	2	10
105	60	24	14	-	2	-	-	-	2	0.6
106	60	24	14	2	-	-	-	-	1	10
107	62	24	14	-	-	-	-	-	3	3
108	54	24	14	-	-	-	2	6	1	10
109	52	24	14	2	-	-	2	6	1	17
110	60	24	8	-	-	-	2	6	2	3
111	54	21.5	12.5	-	-	-	2	10	1	0.5
112	60	21.5	7	-	-	-	2	9.5	2	0.2
113	66	20	8	-	-	-	2	4	1	0.5
114	58	20	14	2	2	-	-	4	1	1
115	70	20	8	-	-	-	2	-	3	0.2
116	70	16	8	-	-	-	2	4	4	0.1

APPENDIX B

APPENDIX B

Glass Properties

Thermal Conductivity, W/m-K, over 310-490 K	0.43-0.74
Density, g/cm^3	2.5-2.8
Description	Blue-Green, Clear-Opaque
Fission Product and Actinide Content, wt%	<0.2
Porosity, vol%	<5
Corrosive Nature	F^-
Softening Point (electrically conductive), ^oC	520-570
Transition Point, ^oC	400-450
Calcine Content, wt%	25-40
Pour Temperature (50-100 poise), ^oC	1100-1150

Practical Frit Composition Range	wt%
SiO_2	55-63
Na_2O	18-26
B_2O_3	8-18
CuO	0-2
CaO	0-3
P_2O_5	0-2
ZnO	0-2
Li_2O	0-2